

# Probing the Charge Distribution at the Electrochemical Interface

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## Abstract

The electrode/electrolyte interface is at the heart of many electrochemical systems and yet gaining insight into the electronic structure at the interface is challenging. Due to its buried nature traditional techniques providing spectroscopic information of localised atoms are difficult to employ. To gain new insight into the charge distribution at the interface we have used resonant surface x-ray diffraction to select the atoms at the interface via the diffraction conditions and obtain spectroscopic information simultaneously. Coupling of the polarisation of the incident x-ray beam with the electron density at the interface allows a direct probe of the charge transfer between the metal electrode and the adsorbing species in the electrolyte solution. Results for the adsorption of halide anions onto Cu and Au single crystal electrode surfaces reveal that there is significant modification of the charge distribution of both the surface and sub-surface atomic metal adlayers in the case of ionic bond formation. This has potential impact both in developing a theoretical understanding of the interface structure and in designing new materials for electrochemical applications.

## 1. Introduction

Electrochemical interfaces are currently of great scientific interest due to their importance for energy technologies, such as in batteries, supercapacitors and fuel cells and other technical applications, for example, in electroplating and sensors. Central to all of these applications is the transfer of electrical charge across the electrochemical interface. For solid-liquid electrochemistry, assessing the charge distribution and charge transfer between the metal electrode and adsorbing species defines the nature of the bonding and is currently understood in only a simplistic way. The rate of the electron transfer defines the reactivity of the material and the performance of any electrochemical device. Electron transfer reactions not only play an important role in electrochemical processes but generally in any chemical reaction. Developing a fundamental understanding of the nature of the charge distribution, especially the influence of the applied potential and the screening by the electrolyte, is thus a major goal.

The issue of 'partial charge transfer' between adsorbates and electrodes has been recently reviewed by Schmickler and Guidelli.<sup>1</sup> They considered the possible electron flow between a molecule (or atom) adsorbing on a metal surface in terms of the overlapping of the metal (M) orbitals with the valence orbitals of the adsorbing molecule (or atom, X). By utilizing the current model of the electrochemical double layer (see Figure 1c) a simplistic understanding of the charge distribution at the interface can be derived. Further insight into the bonding at the electrochemical interface could be obtained by understanding the influence of factors such as screening by water dipoles and partial charge transfer on the M-X dipole moment. As localized charges are always solvated, quantum chemical models must contain a large number of solvent molecules and this is limited by the currently available computing power.

Experimental studies of the charge distribution at the electrochemical interface are

difficult due to the complexity of the electrochemical environment which makes the interface inaccessible to traditional electron-based probes of electronic structure. Typically the charge distribution in materials can be assessed by spectroscopic techniques which probe the bonding energies of the electrons in the material. These techniques include X-ray Photoemission Spectroscopy (XPS) which was traditionally a vacuum-based technique, although using XPS in ambient environments such as high pressure or liquids has recently been achieved but remains challenging.<sup>2, 3</sup> For the study of buried interfaces and bulk materials other x-ray based techniques have been employed successfully. X-ray adsorption spectroscopy (XAS) for example, involves measurements at x-ray adsorption edges at higher x-ray energies and is therefore suitable for studies in ambient environment<sup>4, 5</sup>. The shift of the adsorption edge in the spectra of a specific element is directly linked to the electronic configuration of the atom probed<sup>6, 7</sup>. Site-specificity of a homogeneous sample for these methods can only be achieved indirectly by varying the incident or exit probing angle and using the reflectivity and absorbance of the specimen and, for extended surfaces, this is limited to depth probing. This makes it difficult to isolate the signal from the interface, particularly if the scattering atoms are also present in the electrolyte solution. One way to obtain indirect information of the chemical environment of specific atoms at surfaces or in bulk materials is by measuring the bond length by structural methods, such as x-ray diffraction or Extended X-ray Adsorption Fine Structure (EXAFS), and direct comparison to the bond lengths of bulk materials of known charge states.

Over the last couple of decades x-ray diffraction has been successfully employed to study the atomic structure at the electrochemical interface under operando conditions.<sup>8, 9, 10, 11</sup> The intensity distribution of the diffracted x-rays is probed in reciprocal space, which mathematically is described as the square of the Fourier transform of the electron density of the sample. Due to the abrupt termination and thus step-like change of the electron density,

surfaces and interfaces give rise to a streak like intensity distribution in reciprocal space<sup>12</sup>, the so-called crystal truncation rods (CTRs) which run perpendicular to the surface through the bulk diffraction peaks (Bragg peaks). The intensity at each individual point on the CTRs is directly related to the surface atomic structure and the contribution of individual atoms can be established. Combining x-ray diffraction and x-ray spectroscopy thus seems to be an ideal methodology to access individual local electron density and consequently the charge distribution at specific atoms.<sup>13, 14, 15, 16</sup> In certain circumstances specific surface atoms can be selected by the diffraction conditions. Resonant x-ray scattering in the form of resonant x-ray diffraction or reflectivity has been so far employed to assess element specificity (often referred to as anomalous diffraction).<sup>17, 18</sup> Only in a few cases (e.g. Helliwell)<sup>18</sup> has the methodology been employed to determine the redox state of a specific bonded atom.

We have used *in-situ* resonant surface x-ray scattering measurements on the Cu(001)-halide and Au(001)-halide electrochemical systems in order to directly probe the charge transfer and nature of the chemical bonding. Halide adsorption onto Cu(001) is an ideal system in which to attempt this measurement, as the halide anions, Br and Cl, both form simple ordered c(2x2) adlayers on the Cu(001) surface with adsorption uniquely into the 4-fold Cu hollow site.<sup>19, 20</sup> In the x-ray scattering experiment, the c(2x2) cell gives rise to rods of scattering (superstructure rods) that are separated from the Cu crystal truncation rods (CTR's) in reciprocal space. A schematic of the surface x-ray diffraction features in reciprocal space is shown in Figure 1a. As a result of the symmetry of the surface, the contribution to the superstructure scattering is only due to the halide anion and the second (subsurface) atomic layer of Cu atoms<sup>19</sup>. It is therefore possible to probe independently both the surface Cu atoms, by performing resonant measurements at the Cu K-edge at an 'anti-Bragg' position of a Cu crystal truncation rod (CTR), and the sub-surface Cu atoms (second atomic layer) by performing resonant measurements at the Cu K-edge at the c(2x2) superstructure positions,

i.e. in the latter case the surface Cu atoms do not contribute to the diffracted signal. The Cu-Br system has the advantage that, in addition to the Cu K-edge (8979 eV), the Br K-edge (13474 eV) is also accessible for diffraction measurements. This allows direct probing of the Br adatoms by performing measurements at the Br K-edge. A negative energy shift in the resonance at the Br edge is, to a first approximation, indicative of a negatively charged Br ion due to an induced core level shift.

The paper is organized as follows: in section 2 we explain the experimental methodologies that were used to obtain the resonant surface x-ray diffraction measurements. Section 3 contains the principle results which are selected to highlight the key findings with regard to understanding the charge distribution at the electrochemical interface (additional measurements are contained in the Supplementary Information). These findings are discussed in detail in section 4 with reference to the Cu-halide bonding mechanism.

## **2. Experimental Methods**

The Au(001) single crystal (miscut  $< 0.1^\circ$ ) was prepared by sputtering and annealing in a ultra-high vacuum (UHV) system for several days until a sharp low energy electron diffraction (LEED) pattern showing the ‘hex’ (5x20) reconstruction was observed. The sample was then removed from UHV and, prior to the x-ray experiments, was annealed in a butane flame before cooling in air. The crystal was then transferred to the electrochemical x-ray cell with a drop of ultra-pure water protecting the surface and was immersed at open circuit potential in electrolyte. The experimental procedure followed that of similar studies reported previously. The Cu(001) single crystal sample (miscut  $< 0.1^\circ$ ) was prepared prior to the experiments by electropolishing in 70% orthophosphoric acid. Subsequently, the sample was covered by a droplet of Milli-Q water and mounted into the electrochemical cell. In the experiments 10 mM HCl solution prepared from suprapur hydrochloric acid (Merck) and

Milli-Q water and 10 mM KBr + 10 mM HClO<sub>4</sub> prepared from 99.999% trace metals basis KBr (Aldrich) and 99.999% trace metals basis 70% perchloric acid (Aldrich) were used as electrolyte. All potentials were measured and are quoted versus a Ag/AgCl (3 M KCl) reference electrode.

X-ray measurements were performed on beamline BM28 (XMaS), the UK-CRG beamline at the ESRF, Grenoble using focused incident x-rays. Additional measurements were made on beamline 4-ID-D at the APS, Argonne National Laboratory. The samples were aligned using an incident x-ray beam energy below the Cu K-edge (8979 eV) and Au L<sub>III</sub>-edge (11919 eV) for the copper and gold electrodes respectively. The Au(001) and Cu(001) crystals were indexed to the conventional *fcc* unit cell with the (0, 0, L) direction along the surface normal ( $a^*=b^*=c^*=2\pi/a$ , where  $a=4.078$  Å and  $a=3.615$  Å, for Au(001) and Cu(001) respectively) and aligned with the (0, 0, 2) and (1, 1, 1) bulk Bragg reflections. A schematic of the intensity distribution in reciprocal space is shown in Figure 1a. The resonant data were recorded on specific points in reciprocal space by scanning the energy through the adsorption edge and keeping the Q-vector constant. Further details regarding the energy resolution and the separation of the elastic and fluorescent signals are given in the supplementary information (section S1 and Figure S1). On BM28, two different geometries were employed: the vertical geometry in which the Q-vector is perpendicular to the polarization of the x-ray beam, thus for in-plane positions (at low L) the polarization of the beam is parallel to the surface normal and the horizontal geometry in which the Q-vector is parallel to the polarization of the x-ray beam, thus for in-plane positions (at low L) the polarization of the beam is perpendicular to the surface normal. The fluorescence signal from the copper substrate was recorded in parallel to the resonant surface x-ray diffraction measurements and its derivative is used to define the exact position of the Cu K-edge (Figure 2a). For the Br K-edge, the fluorescence data were also recorded in parallel to the resonant surface diffraction

signal (Figure 3a). In this case, however, the Br fluorescence is dominated by the Br ions in solution and does not give the exact position of the Br edge, therefore the Br edge data were always measured in horizontal and vertical polarization to extract any surface induced asymmetry of the charge distribution. Due to the relatively small scattering intensity obtained in the measurements, each energy and background scan was repeated at least once to allow for averaging. The scans were repeated to acquire sufficiently precise counting statistics. In all measurements, the outer chamber of the x-ray cell was continuously purged with nitrogen to protect the surfaces from oxygen. A schematic of the electrochemical cell and the two different polarisations of the x-ray beam are shown in Figure 1b.

### 3. Results

For the Cu(001)-c(2x2)-Cl superstructure the intensity on the (1, 1, L) CTR was recorded while scanning through the Cu-K-edge at L=0.2, 0.6 and 0.8. These experiments were performed in a vertical scattering geometry, which has the polarization of the X-ray beam normal to the surface. The polarisation with respect to the crystal surface in the electrochemical cell is shown schematically in Figure 1b. The results obtained at L=0.2, which is close to the ‘anti-Bragg position’ where there is maximum sensitivity to the surface Cu atomic layer.<sup>19</sup>, are shown in Figure 2c and indicate a shift in energy of the edge towards higher energy. This result can be modelled by a shift of the Cu K-edge associated with the first atomic layer of Cu atoms to higher energies by  $\Delta E = 5.5 \pm 0.5$  eV (red line in Figure 2c). A simple adsorption edge profile was assumed and any fine structure or EXAFS features are not included in the calculation<sup>21</sup>. For clarity the scans at higher L are not shown in Figure 2c (for detail, see supplementary information, Figure S2). The same measurement was performed for the Cu(001)-c(2x2)-Br system (supplementary information, Figure S4) and this also exhibited a shift in the edge position of  $\Delta E = 2.5 \pm 0.5$  eV. In contrast identical measurements at the (1,

1, 0.2) CTR position recorded in a horizontal scattering geometry (which has the polarization of the x-ray beam parallel to the surface-as shown in Figure 1b) exhibited no shift in the Cu K-edge position.

Due to the extra symmetry of the c(2x2) adlayer, scattering uniquely due to this superstructure occurs and is separated from the CTRs (blue lines in Figure 1a) in reciprocal space. As stated in the introduction, due to symmetry the contribution to the superstructure scattering is only due to the halide anion and the second (subsurface) atomic layer of Cu atoms<sup>19</sup>. For both the Cu(001)-c(2x2)-Cl and Cu(001)-c(2x2)-Br superstructure the intensity at the (0, 1, L) superstructure rod at L=0.2 was recorded in vertical scattering geometry while varying the incident x-ray energy through the Cu K-edge (Figure 2b). The same response was obtained in vertical scattering geometry for the Cu(001)-c(2x2)-Br system at this position. In both systems no dependence on the polarisation of the incident x-ray beam was observed. For the halide-free Cu(001) surface there is no scattering as this reciprocal space position is forbidden when the c(2x2) superstructure is not present. Thus no energy dependence while scanning through the Cu K-edge is expected unless the electron density of the copper atoms has the symmetry of the c(2x2) superstructure; in this case the second Cu atomic layer contributes to the c(2x2) structure because it is buckled.<sup>19</sup> The different energy dependencies of the diffracted intensity, as expected from a shift of the Cu K-edge for the Cu atoms in the second atomic layer, were modelled and are shown in Figure 3b. The blue line represents a uniform position of the K-edge for both Cu sites (the one beneath the halide anion and the one beneath a free hollow site). Only by inducing a shift in the Cu K-edge position between the two atomic Cu sites can the experimental data be reproduced. The Cu atom directly below the Cl ion has a Cu K-edge shifted towards higher energies by  $\Delta E = 7.5 \pm 0.5$  eV whereas the Cu atom below an unoccupied hollow site is shifted by  $\Delta E = 1.5 \pm 0.5$  eV. In addition to the measurements at the Cu K-edge, for the Cu(001)-c(2x2)-Br superstructure the intensity at the



superstructure position, (0, 1, 0.2), was recorded while scanning through the Br K-edge (Figure 3b). In this case the data were recorded in vertical and horizontal geometry to be able to distinguish the effect of the charge transfer between the adsorbed Br ion and the electrode surface. A clear shift of the Br K-edge towards lower energy,  $\Delta E = 3.0 \pm 0.5 \text{ eV}$ , can be observed in the vertical scattering geometry, i.e. with the x-ray polarisation normal to the surface.

For comparison to the data obtained for halide adsorption onto Cu(001), resonant surface x-ray diffraction data for bromide adsorption onto Au(001) were also recorded. Bromide forms a  $c(\sqrt{2} \times 2\sqrt{2})R45^\circ$  superstructure on Au(001) in a potential range between 0 V and 0.4 V in 10 mM KBr + 0.1 M HClO<sub>4</sub><sup>22</sup>. Data were measured on the superstructure rod, at (0.5, 1, 0.2), by scanning the x-ray energy through the Br K-edge (Figure 3c) and at the surface sensitive CTR ‘anti-Bragg’ position, (1, 1, 0.2), by scanning the x-ray energy through the Au L<sub>III</sub>-edge (supplementary information, Figure S5). No shift in either the Br K-edge or the Au L<sub>III</sub>-edge position is observed and, furthermore, there is no difference between the results measured in both horizontal and vertical scattering geometries.

#### 4. Discussion

Resonant surface x-ray diffraction measurements were recorded from the Cl and Br  $c(2 \times 2)$  adsorbate structures on Cu(001) and the Br  $c(\sqrt{2} \times 2\sqrt{2})R45^\circ$  adsorbate structure on Au(001), by varying the x-ray energy through the Cu K-edge (Au L<sub>III</sub> edge) or Br K-edge whilst maintaining the diffraction conditions at particular reciprocal lattice points. For the halide adsorbates on Cu(001), a clear shift of the Cu K-edge spectrum towards higher energies can be observed at surface sensitive positions. This can be interpreted by a positive charge contained in the Cu surface atoms which are contributing to the bonding of the halide. A general shift of the Cu K-edge depending on the charge has been recorded previously<sup>23, 24, 25</sup>. The shift is assigned to a change of the Cu 1s energy level. For the subsurface Cu atoms in

the second atomic layer the shift of the Cu K-edge can be simply assigned to a positive charge remaining on the atom, as no polarisation dependence is observed. Correlation between an edge shift and charge on the atom has been established previously and with a shift of 7 eV, assigned to the Cu atom, this would correspond to a positive charge of 1 e on the Cu atom directly below the chloride atom, whereas the Cu atom in the second atomic layer, below an unoccupied hollow site, exhibits only a shift of 1.5 eV corresponding to a positive charge of 1/3 of 1 e. To establish an understanding of the polarisation dependence observed, the symmetry of the orbitals involved in the electron transfer and the x-ray absorption process have to be considered. The electron excitation process together with the alignment of the polarisation with the (001) surface and electronic states of the copper are depicted in Figure 4 (note that the filled states are shown by electron spin pairs, this is a representation and no link to the coordinate system of the surface or polarisation shown in the figure is to be assumed). The symmetry of the initial state (1s) and possible final states (3d, 4s and 4p) together with the corresponding orientation of the Cu surface and the two polarisations of the x-rays employed in this study are indicated. Due to the symmetry of the s-orbitals the polarisation dependence of the edge position at the same position in reciprocal space cannot be explained by a modification of the core 1s level neither through a surface core level shift nor through a shift due to ionisation as observed in copper complexes.

As x-ray absorption is probing the empty states (grey background in Figure 4), the effect of a charge modification on a specific Cu atom has to be considered to explain the polarisation dependence. The 1s to 3d transition is a weak quadrupole transition and the edge of the K-edge stems from the 1s to 4s/4p transition. The polarisation dependence observed thus has to be a lifting of the degeneracy of the 4p electronic states, more precisely the 4p<sub>z</sub> state is shifted with respect to the 4p<sub>x</sub> and 4p<sub>y</sub> states, either due to a modification of the neighbouring d-orbitals resulting in a charge asymmetry or due to a partial charging of the p-

orbitals. The uncharged Cu atom has a  $3d^{10}4s^1$  electron configuration. Hence a (partial) positive charge of the Cu atom can either stem from the removal of an electron from the 3d or 4s orbitals. A positively charged or delocalised d-orbital would result in a more localised p-orbital, resulting in a shift of the energy levels to lower energies observable through a shift to lower energies in the adsorption K-edge; this would not explain our results. A transfer of the 4s electron to the more delocalised p-orbitals, in this case specifically the  $p_z$  orbital, would result in a partial positive charge of the Cu atom with the  $p_z$  electron contributing to the ionic bonding of the Br anion and in a shift of the energies of the now partially occupied Cu  $3p_z$  orbital to higher energies with respect to the Cu  $3p_x$  or  $3p_y$  orbitals. This charge transfer and the resulting lifting of the degeneracy of the p-orbital are indicated in Figure 4 through the green arrow representing the electron moved from the 4s to the  $4p_z$  orbital. Such a degeneracy of the p orbitals would be observable in the polarisation dependence measurement of the Cu K-edge. The x-rays polarised along the surface normal of the electrode excite the 1s electrons to the  $4p_z$  orbital, which is shifted to higher energies with respect to the  $p_x$ ,  $p_y$  orbitals, thus resulting in the positive shift in the Cu K-edge that is observed.

For Br adsorbed on Cu(001) in UHV the main bonding has been found to be through a Cu 4s and  $3d_z^2$  interaction<sup>26</sup> which, as discussed in the previous paragraph, cannot explain the experimental results presented here. The structure of halide anions on Cu(001) under UHV conditions has been shown to be different from that in electrochemical environment, with a bond length of the halide atom to the copper atoms closer to that expected for a covalent bond than an ionic bond<sup>19, 27</sup>. The difference in the bonding seems to stem from the difference in the orbitals (2d versus 3p) contributing to the bonding. The 3d orbitals contribute together with the 4s orbital to the bonding in UHV.<sup>26</sup> In the electrochemical environment the p-orbitals, which are less localised and directional than the 3d orbitals, contribute to the

bonding resulting in a less localised and directed bonding with the p-orbital more overlapping the Br electron density. Thus this type of bonding involving a ‘partial’ charge transfer is perceived as more ionic. For the Br K-edge the assignment of the edge shift to the chemical state of the Bromine atom<sup>28</sup> is less well established. For Br adsorbed on Cu(001) in UHV a contribution of the Br 4p<sub>z</sub> orbital was found. Similar to the argumentation used to explain the Cu K-edge shifts the difference in the polarisation dependence arises from the asymmetry of the charge distribution at the electrode surface.

The discussion above is kept simplistic to draw basic conclusions on possible charge shifts without any further theoretical modelling. For a more rigorous interpretation of the data hybridisation of the orbitals of the surface atoms (copper and bromine) and the associated shift in energies and lifting of the degeneration would have to be considered. This is beyond the scope of this article.

## 5. Conclusion

In this article we have shown how resonant surface x-ray diffraction can be used to probe the details of the charge distribution at the electrochemical interface. This was illustrated by measurements of halide adlayers on single crystal Cu(001) and Au(001) electrodes in which the bonding at the electrochemical interface is known to be different from that observed under UHV conditions. The results clearly point to the need of a revision of the model of the charge distribution at electrochemical interfaces. So far either Jellium (for metal electrode) or tight bonding (specific oxidation state) models have been employed. The results presented here indicate, however, a potential drop extending at least into the 2<sup>nd</sup> atomic layer of the metal. Our results clearly show that the surface of the electrode can exhibit a difference in the electronic density around atoms related to specific adsorption. This is taking the challenge for theorists to the next level as not only the applied potential and charge

distribution in the double layer region should be considered but also that the current self-consistent modelling approaches to account for (sub-)surface charges need to be modified in order, for example, to pull out the differences between an electrochemical and a UHV environment. Both experiment and theory have shown that the electronic structure at the surfaces of novel materials that have been designed for electrochemical applications, e.g. electrocatalysis, is crucial in determining the enhanced activity for a specific reaction <sup>29</sup>. The precise atomic charge distribution on such material surfaces will have an impact not only on activity but also on their stability during the electrocatalytic reaction <sup>30</sup>. Thus the current approach for the design of electrochemical systems will have to consider surface charges even on relatively simple metal electrodes. The ability to understand the potential-dependent charge distribution would be particularly relevant in the development of more complex electrode surfaces, for example, bimetallic or perovskite materials for electrocatalytic applications.

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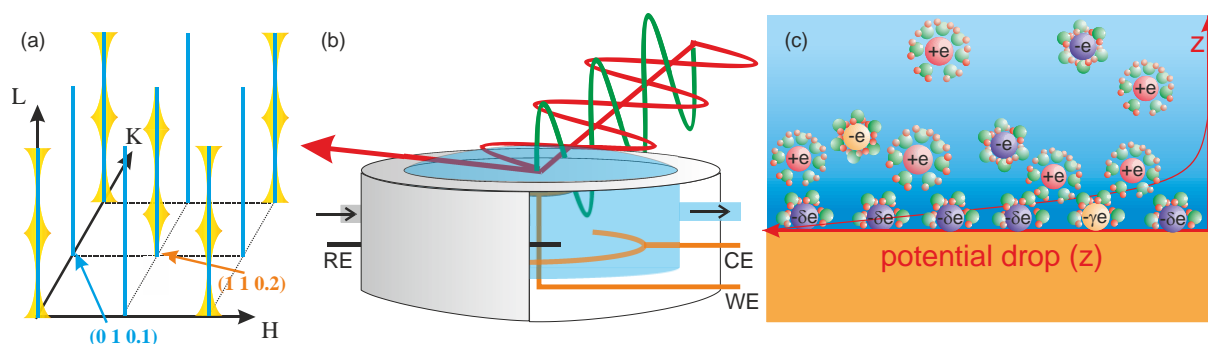
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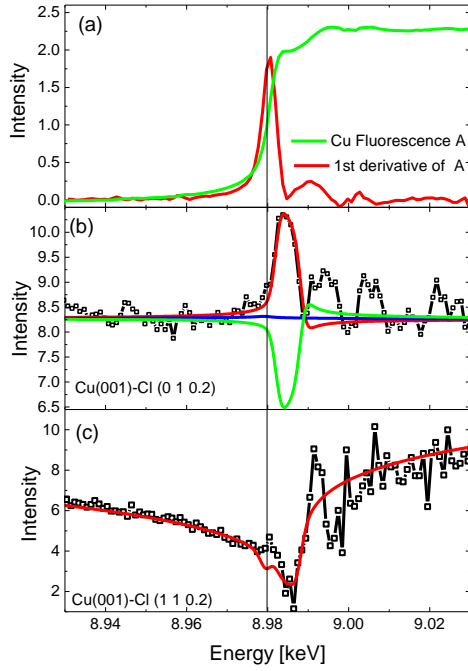
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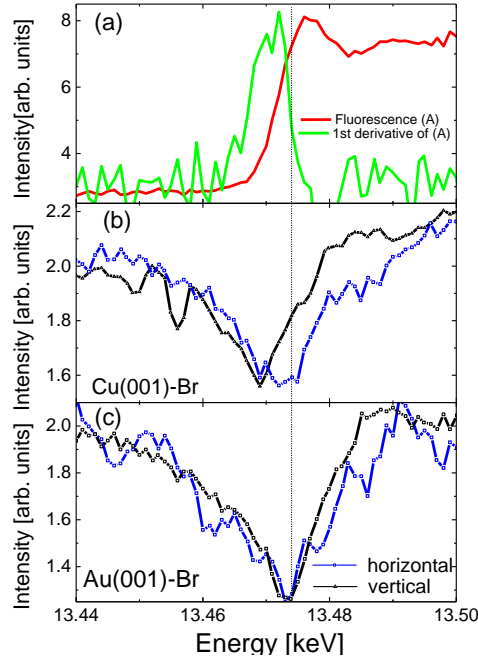


**Figure 1.** Figure 1a depicts the reciprocal space of the Cu(001)-c(2x2)-Cl system, which is the principal model system used in this study of the charge distribution at the electrochemical interface by resonant surface x-ray diffraction. The electrochemical cell and the two polarisations of the incident x-ray beam, normal to the surface (green line) and in the surface plane (red line), are shown in Figure 1b. Figure 1c shows a model of the electrochemical interface with the ions in solution and adsorbed on the surface and the current understanding of partial charges together with the potential drop across the interface.

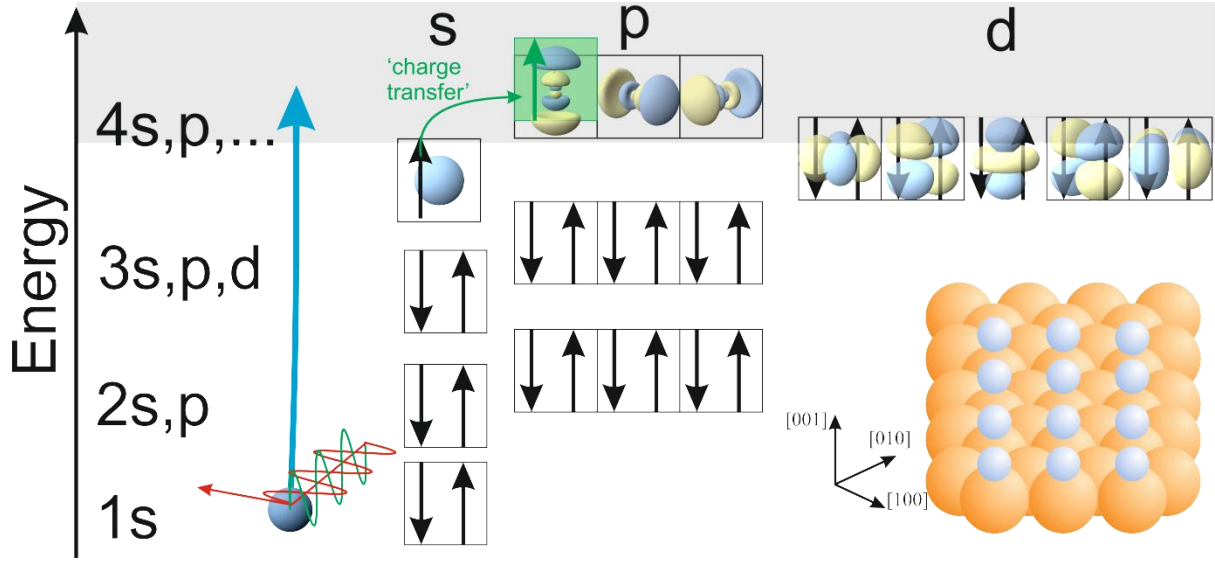


**Figure 2.** Resonant surface x-ray diffraction data measured at the Cu K edge from the Cu(001)-c(2x2)-Cl structure. The fluorescence signal recorded in parallel to the resonant x-ray diffraction measurements and its derivative are shown in (a), which defines the position of the Cu K-edge. (b) The elastically scattered x-ray signal measured at (0, 1, 0.2), a position on the rod of scattering that is uniquely due to the c(2x2) structure and (c) The elastically scattered x-ray signal measured at (1, 1, 0.2), a surface sensitive position on the crystal truncation rod (CTR) arising from the termination of the Cu lattice. The edge position is indicated by the black vertical line. All data were measured in a vertical scattering geometry, i.e. with the polarization of the x-ray beam perpendicular to the sample surface normal. Calculations of the scattered intensity according to a simple model (red line) in (b) and (c) for the specific Cu edge shifts. The blue line in (b) is a calculation with no relative shift in the edge of the Cu atoms in the second atomic layer. The red line is the model for a more positive shift of the K-edge for the Cu atom directly below the Cl atoms with respect to the Cu atom directly below an unoccupied site. The green line is the calculated intensity for the inverse

scenario.



**Figure 3.** Resonant surface x-ray diffraction data measured at the Br K-edge. Data were measured at positions on the rods of scattering that arise due to the superstructures (b) Cu(001)-c(2x2)-Br (measured at (0, 1, 0.2)) and (c) Au(001)- $c(\sqrt{2} \times 2\sqrt{2})R45^\circ$ -Br (measured at (0.5, 1, 0.2)) for incident x-rays with horizontal (blue) and vertical (black) polarisation with respect to the surface normal. In addition to the elastically scattered x-ray signal recorded at  $L=0.2$ , the Br fluorescence was recorded in parallel and its derivative is shown in (a). The fluorescence arises from the Br ions in solution, which are charged and fully solvated, and is thus not a good indication of the exact position of the Br K-edge. The exact position of the Br K-edge is indicated by the dashed line.



**Figure 4.** A schematic of the energy levels of the Cu atoms in the first atomic layer. The Cu(001)-c(2x2)-halide structure (surface Cu layer and adsorbed halide) is shown schematically in the inset with the same coordinate system as the polarisation of the x-rays shown and the orbitals depicted in the energy diagram. When scanning the Cu K-edge, Cu 1s core electrons are excited to energies corresponding to the free states or vacuum level, depicted by the grey background in the picture. The two different polarisations of the exciting x-rays are shown in the figure. The orbitals for the non-symmetric final states are depicted as they are the key to understanding the polarisation dependence reported in this article. The first free allowed transition is to 4p orbitals. The lifting of the degeneracy of the p-orbitals due to an occupation of the  $p_z$  orbital with possibly the original 4s electron is depicted in the Figure. Further details are discussed in the text.